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6. AUTHOR(S) Alan J. Heeger			
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Due 28, February 1996**

to

**Air Force Office of Scientific Research**

**F49620-93-1-0191DEF**

**Conjugated Polymers with Degenerate Ground State:  
The Route to High Performance NLO Response**

**Principal Investigators:**

Professor Alan J. Heeger  
Professor Fred Wudl

**Administering Unit:**

Institute for Polymers and Organic Solids  
University of California at Santa Barbara  
Santa Barbara, CA 93106

19961015 031

## **I. Objectives:**

This program of scientific research is focused on the nonlinear optical properties of conjugated polymers with a particular emphasis on Conjugated Polymers with Degenerate Ground State: The Route to High Performance NLO Response. During the final year there was a shift in emphasis toward the use of Photoinduced Electron Transfer in Conducting Polymer - Fullerene Composites as a Route to High Performance NLO Materials.

The program had three goals:

- The use of conjugated polymers with degenerate ground state as a route to high performance third order NLO
- The development of a prototype optical correlators and the demonstration of optical computing based on the following two classes of materials:
  - a. Conjugated polymers with degenerate ground state polymer
  - b. Photorefractive materials
- The development of Photoinduced Optical Limiters based on Conducting Polymer - Fullerene Composites

Each of these represented a novel and potentially important NLO materials concept.

## **II. Summary of Progress (Final Report)**

### **A. The use of conjugated polymers with degenerate ground state as a route to high performance third order NLO**

The work on the first goal was successfully completed. We demonstrated unusually large third order NLO coefficients in the class of conjugated polymers with degenerate ground state, and we verified that the mechanism is the result of the virtual soliton pair intermediate states. These results are presented in detail in the following publications:

Frequency dependence of third harmonic generation in cis and trans polyacetylene: importance of degenerate ground state to nonlinear optical response

C. Halvorson, D. Moses, T.W. Hagler, Y. Cao and A.J. Heeger, Synth. Met. 49-50, 49 (1992)

Conjugated polymers with degenerate ground state: The route to high performance third-order nonlinear optical response

C. Halvorson, T.W. Hagler, D. Moses, Y.Cao and A.J. Heeger, Chem. Phys. Lett. 200, 364 (1992)

Soluble conjugated polymers with degenerate ground state: Derivatives of poly(1,6-heptadiyne)

K. Pakbaz, R. Wu, F. Wudl and A.J. Heeger, J. Chem. Phys. 99, 590 (1993)

Third harmonic generation spectra of degenerate ground state derivatives of poly(1,6-heptadiyne)

C. Halvorson, R. Wu, D. Moses, F. Wudl and A.J. Heeger, Chem. Phys. Lett. 212, 85 (1993)

Two-photon absorption spectrum of oriented trans-polyacetylene

C. Halvorson and A.J. Heeger, Chem. Phys. Lett. 216, 488 (1993)

Third harmonic generation spectra of degenerate ground state poly[(dipropargyl) amines]

J. McElvain, N. Zhang, C. Halvorson, F. Wudl, and A.J. Heeger, Chem. Phys. Lett. 232, 149 (1995)

Third harmonic generation spectrum of a degenerate ground state polymer: Direct evidence of simultaneous two- and three-photon resonance  
J. McElvain, M. Cha, H. Yu, N. Zhang, F. Wudl and A.J. Heeger, Chem. Phys. Lett. 247, 221 (1995)

**B. The development of a prototype optical correlators and the demonstration of optical computing based on the following two classes of materials:**  
a. Conjugated polymers with degenerate ground state  
b. Photorefractive materials

The work on the second goal was successfully completed, both using conjugated polymers with degenerate ground state and using photorefractive polymers as the active materials. This progress was reported in detail in the following publications:

A 160 femtosecond optical image processor based on a conjugated polymer  
C. Halvorson, A. Hays, B. Kraabel, R. Wu, F. Wudl and A.J. Heeger, Science, 265, 1215 (1994)

Optical computing by use of photorefractive polymers  
C. Halvorson, B. Kraabel, A.J. Heeger, B.L. Volodin, K. Meerholz, Sandalphon and N. Peyghambarian, Optics Letters, 20, 76 (1995)

Femtosecond optical correlation using four-wave mixing  
C. Halvorson, A. Hays, B. Kraabel, R. Wu, F. Wudl and A.J. Heeger, Synth. Met. 71, 2197 (1995)

Two-photon absorption and Ultrafast optical computing  
C. Halvorson and A.J. Heeger, Synth. Met. 71, 1649 (1995).

This work was expanded with the goal of demonstrating a compact, low cost version of the optical correlator. This aspect was completed (during the summer of 1996) and submitted to Rev. Sci. Instruments as follows:

Compact, low power polymer-based optical correlator  
D. Vacar, A.J. Heeger, B. Volodin, K. Kippelen and N. Peyghambarian, Rev. Sci. Inst. (submitted).

**C. The development of Photoinduced Optical Limiters based on Conducting Polymer - Fullerene Composites**

Major progress was made toward the third goal as summarized in the following publication:

Enhanced nonlinear absorption and optical limiting in semiconducting polymer/methanofullerene charge transfer films  
M. Cha, N.S. Sariciftci, A.J. Heeger, J.C. Hummelen and F. Wudl, Appl. Phys. Lett. 67, 3850 (1995).

This work has opened an entirely new direction for research on nonlinear optical materials; it forms the basis for the renewal contract which began in early 1996. More recent progress in this area is particularly promising. In fact charge-transfer polymers have been shown to be a new class of nonlinear optical materials which can be used for generating femtosecond holographic gratings with high diffraction efficiencies.

### **D. Polymer Grid Triodes**

An analytic model was developed for the polymer grid triode. Analysis of the generalized field assisted carrier injection by tunneling, controlled by the grid voltage, resulted in the development of a successful description of the charge injection and transport in the polymer grid triode. The results have been accepted for publication.

An analytic model of the polymer grid triode  
J. McElvain and A.J.Heeger, J. Appl. Phys. (in press).

All aspects of the experimental equipment and procedures are included in the publications listed above.

### **III. Advanced degrees awarded**

Dr. Craig Halvorson  
Dissertation title: "Third Order Nonlinear Optical Effects in Conjugated Polymers"

Dr. Andrew Hays  
Dissertation title: "Ultrafast All-Optical Phenomena and Devices Using Conjugated Polymer Thin Films"

### **IV. Cumulative list of researchers involved in the AFOSR research effort**

Craig Halvorson, Research Physicist  
Francois Brown de Colstoun, Research Physicist  
Andrew Hays Graduate Student & Research Physicist  
Myounsik Cha, Research Physicist  
Daniel Moses, Research Physicist  
Changhee Lee, Graduate Student  
Reghu Menon, Research Physicist  
Serdar Sariciftci, Research Physicist  
Laura Smilowitz, Graduate Student  
Jean-Luc Brédas, Research Physicist  
Helen Nugent, Research Chemist  
Ruilan Wu, Research Chemist  
Hailiang Wang, Research Chemist  
Gordana Srdanov, Staff Research Assoc., Physical Chemist  
Paul Smith, Professor  
Fred Wudl, Professor, co-P.I.  
Alan J. Heeger, Professor, P.I.